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POLYCYCLIC AROMATIC HYDROCARBONS IN A HIGHLY INDUSTRIALIZED URBAN ESTUARY: INVENTORIES AND TRENDS

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Abstract—The abundance and composition of polycyclic aromatic hydrocarbons (PAHs) in sediments of the main stem and southern branch of the Elizabeth River (VA, USA), a highly industrialized urban estuary in the Chesapeake Bay (USA) watershed, were examined relative to historical and toxic effects levels. Total PAH concentrations in Elizabeth River sediments exceeded those observed in Baltimore Harbor and the Anacostia River, two other regions of concern in the Chesapeake Bay. The ΣPAH concentrations from samples collected in the vicinity of two former wood-treatment facilities in the Elizabeth River had the highest ΣPAH when compared to coastal and estuarine systems around the world. Using a linearized diffusion model equation, as much as 69% of the variability in channel sediment ΣPAH distribution could be ascribed to inputs associated with former wood-treatment facilities along the southern branch of the Elizabeth River. Comparison of PAH levels measured in channel samples to data collected during the early 1980s demonstrated a general trend toward reduction in contaminant concentrations for most regions of the Elizabeth River channel; however, steady-state and increased sediment PAH concentrations in the vicinity of the former wood-treatment facilities were observed. Based on examination of the contaminant levels in Elizabeth River sediments using established sediment-quality criteria, the southern branch of the river remains a clear hazard to benthic and pelagic organisms.

Keywords—Polycyclic aromatic hydrocarbons Sediment Elizabeth River Effects levels Particle interactions

INTRODUCTION

The Elizabeth River (VA, USA), which is part of the Chesapeake Bay (USA) estuarine system, is one of three regions of concern identified by the U.S. Environmental Protection Agency in its Chesapeake Bay Program (http://www.chesapeakebay.net/bayfaq.htm). The Elizabeth River is a subestuary of the James River, which is the southernmost tributary of the Chesapeake Bay. Initially a drowned-river, marsh-lined estuary [1], significant alterations of the subestuary began in the mid-1700s, with the construction of shipbuilding and repair facilities. Large-scale development of the area began in the 1880s, with the onset of coal storage and transport. Subsequently, the main stem and southern branch of the Elizabeth River have been used for naval shipyards, coal storage and transport, petroleum distribution and shipment, and wood treatment [2,3]. A minimum of three and, potentially, as many as five wood-treatment facilities were present on the southern branch of the Elizabeth River [3–5]. The three known wood-treatment facilities began operation in the early 1900s and continued until the last was shut down in 1981. Industrial wastewater dumping from these facilities was banned in 1968, but these sites may represent continuing sources of contaminants because of the leakage of creosote from land-based dumpsites, storage facilities, or general spills [5]. In addition to military and industrial facilities, the Elizabeth River as a whole is surrounded by the cities of Norfolk, Chesapeake, and Portsmouth (VA, USA), all urban areas with associated commercial and residential development (Fig. 1).

Because of the extensive shoreline development of the Elizabeth River, its hydrodynamic response is different from that of a naturally configured river basin. This development has multiple impacts, including increasing the residence time of dissolved and particulate contaminants through the lengthening of the river via construction of the Craney Island dredge spoil disposal area (Portsmouth, VA, USA) [6]. Development and alteration of the shoreline also reduced the tidal flow from the James River (USA) [1] and restricted the ebb flow from the Elizabeth River such that it favors the Norfolk shoreline and largely returns to the Elizabeth River on the following flood tide [7,8]. Freshwater input from the Dismal Swamp (USA), the only freshwater source, is also restricted because of a series of locks and a spillway located at Deep Creek (VA, USA) [8]. Deepening of shipping channels in the main stem and the southern branch has increased the frequency and degree of dredging these areas such that between 1956 and 1982, approximately 1.0 to 1.5 million m^3/year of sediment were removed from the river [1]. Despite this high rate of dredging, point- and nonpoint-source contamination of Elizabeth River sediments remains prevalent.

The degree and type of industrialization on the Elizabeth River has led not only elevated levels of contaminants but also to a variety of contaminants and sources. Four Superfund National Priorities List sites are currently active immediately adjacent or in close proximity to the Elizabeth River, whereas as many as five non–National Priorities List Superfund sites may also exist in the vicinity of the Elizabeth River, with varying states of contamination and remediation (http://www.epa.gov/superfund/sites/cursites/vacerlst.htm). Multiple potential sources of polycyclic aromatic hydrocarbons (PAHs) exist on the Elizabeth River in the form of coal and petroleum

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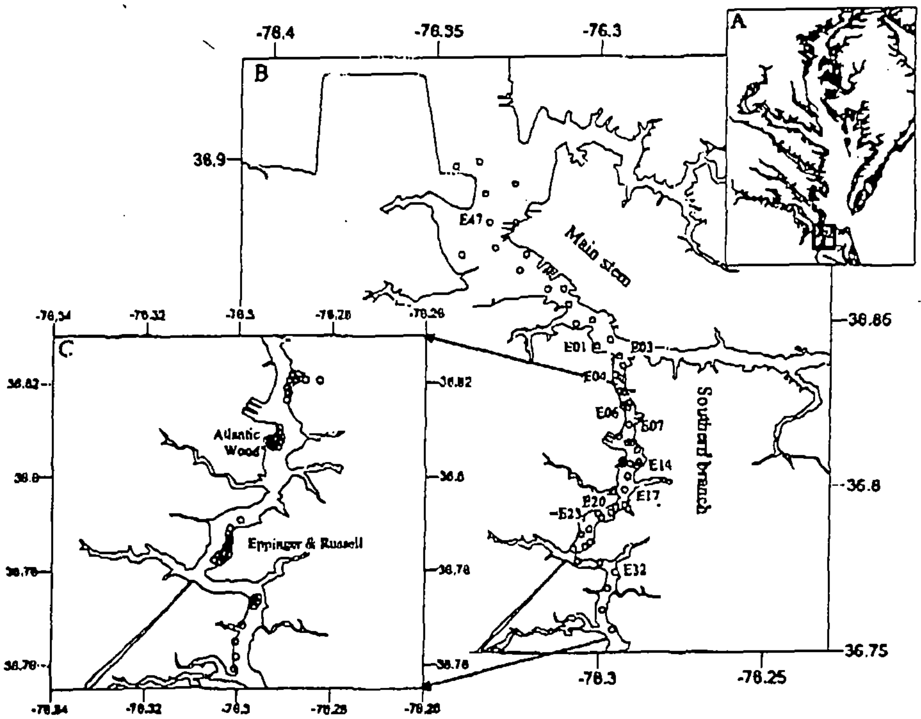

Fig. 1. (A) Elizabeth River (VA, USA): Study site (within highlighted box) in the Chesapeake Bay system. (B) Locations of samples collected in 1998. An additional eight samples collected in 1999 to complete the geographic survey of the river are also included. (C) Locations of samples collected in 1999. Identified sample locations are discussed in the text.

storage and transport facilities, wood-treatment areas, and shipbuilding and repair activities.

Although the Elizabeth River has been the subject of public scrutiny in recent years, intensive scientific investigation has been intermittent. Previous investigations of the Elizabeth River have focused mainly on the general trends in sediment PAH concentrations, often coupled with associated toxicological impact to benthic and pelagic species [2,4,9,10]. Merrill and Wade [5] attempted to fingerprint contaminated sediments using suspected PAH and *n*-alkane source signatures. They concluded that historical creosote releases and weathered petroleum products dominated the sediment contamination. More recently, Walker and Dickhut [11] examined PAH isomer distributions in sediments from the main stem and southern branch of the Elizabeth River relative to two suspected source areas (specifically, two former wood-treatment facilities on the southern branch). In addition to these sources, coal and/or a former coal gasification plant was found to be a primary source of PAHs to the main stem of the river. The goal of the present study was to assess the current state of the Elizabeth River subestuary, specifically regarding levels of PAHs in sediments.

MATERIALS AND METHODS

Sample collection

Fifty-one surface sediment samples were collected from the main stem and southern branch of the Elizabeth River on June 9–11, 1998 (Fig. 1B). These samples were collected adjacent to Craney Island and along the main stem into the southern branch, with the total extent of the sample area extending approximately 22 km from the mouth of the Elizabeth River. Twenty-nine samples were collected within the active dredge channel, and 21 samples were collected from both the eastern and western shoal areas. In July 1999, an additional 62 shoal samples were collected in the southern branch (Fig. 1C). Eight of these samples completed the geographic coverage of the 1998 shoal samples (Fig. 1B); the remaining samples targeted suspected or potential PAH source areas in the southern branch.

All sediment samples were collected using a Smith-MacIntyre surface grab sampler (Ocean Instruments, San Diego, CA, USA). The top 2 cm of sediment were removed using a solvent-rinsed, metal spatula and then placed in precleaned, ashed (4 h at 400°C), glass jars with ashed, aluminum-lined lids for transport and storage. In four shoal locations, a separate sediment sample of the 2- to 4-cm layer was collected in addition to the surface sediment. Within 24 h of collection, the samples were centrifuged at 1,500 rpm for 25 min to remove sediment pore water (for later analysis). The remaining sediment was stored in a cold room at 4°C until analysis.

Sample extraction

Sediment samples were homogenized and subsampled for subsequent analyses (i.e., grain size, water content, and PAH analysis). Approximately 10 g of sediment were transferred to an aluminum weighing pan to measure the percentage of moisture. The subsample was weighed and allowed to dry at 60°C for a minimum of 48 h. The samples were then allowed to cool briefly and reweighed to ±0.1 mg.

Approximately 7 to 12 g of sediment were used for PAH analysis. The samples collected in 1998 were extracted in the following manner: A subsample was placed in an ashed, solvent-rinsed, 8-ounce Qorpak® (Bridgeville, PA, USA) jar and then weighed. Thirty milliliters of a 1:1 acetone:dichloromethane (DCM) solvent mixture were added to each sample in addition to a surrogate standard mixture containing deuterated PAHs (d_{10}-anthracene, d_{12}-benz[*a*]anthracene, d_{12}-benzo[*a*]pyrene, and d_{12}-benzo[*ghi*]perylene). A sample-weight equivalent of precleaned and dry Na_2SO_4 was also added to each jar, and sediments were then extracted three times with

Table 1. Percentage difference of sample concentrations calculated from the sonication extraction and accelerated solvent extraction (ASE) of National Institute for Standards and Testing (NIST) Standard 1944 Reference Material (SRM)[a]

Polycyclic aromatic hydrocarbon	SRM 1944	95% Confidence interval	Sonication (*n* = 2)	Standard deviation	% Difference	ASE (*n* = 2)	Standard deviation	% Difference
Phenanthrene	5.27	0.22	3.50	0.12	−33.64	4.52	1.19	−14.30
Anthracene	1.77	0.33	0.80	0.01	−54.72	1.16	0.14	−34.29
Fluoranthene	8.92	0.32	8.30	3.02	−6.91	7.06	1.27	−20.82
Pyrene	9.70	0.42	7.59	2.70	−21.80	7.29	1.37	−24.80
Benz[*a*]anthracene	4.72	0.11	2.99	0.08	−36.75	3.44	0.74	−27.13
Chrysene	4.86	0.10	2.98	0.16	−38.61	3.34	0.72	−31.29
Benzo[*b*]fluoranthene	3.87	0.42	4.01	0.01	3.57	5.02	1.47	29.68
Benzo[*k*]fluoranthene	2.30	0.20	1.46	0.04	−36.37	1.87	0.51	−18.63
Benzo[*e*]pyrene	3.28	0.11	2.59	0.05	−21.14	3.46	0.92	5.52
Benzo[*a*]pyrene	4.30	0.13	2.85	0.14	−33.66	3.79	1.16	−11.92
Perylene	1.17	0.24	0.84	0.08	−28.03	0.98	0.06	−16.62
Benzo[*ghi*]perylene	2.84	0.10	2.08	0.10	−26.88	2.48	0.61	−12.68
Indeno[1,2,3-*cd*]pyrene	2.78	0.10	3.02	0.06	8.60	3.42	0.71	23.02

[a] Percentage difference was obtained using average values from the sonication and ASE extractions relative to expected values reported for NIST standard (*http://patapsco.nist.gov/srmcatalog/certificates/1944.pdf*).

the acetone:DCM solvent mixture (once with 30 ml and twice with 20 ml) for 45 min in an ultrasonic bath. After each extraction, the sample was centrifuged at 1,200 rpm for 20 min. The extract was then transferred to another flask for sample reduction and solvent exchange into hexane via rotary evaporation.

The samples collected in 1999 were extracted using pressurized fluid extraction (denoted here as accelerated solvent extraction [ASE]; Dionex ASE 200 Accelerated Solvent Extractor, Sunnyvale, CA, USA). A 7- to 8-g subsample, along with surrogate standard mixture, was mixed with a sufficient amount of Hydromatrix® (Varian, Walnut Creek, CA, USA) to facilitate water removal and adequate wetting of the sediment surface with organic solvents. The sample was then subjected to high-temperature (100°C), high-pressure (2,000 psi) extraction with 1:1 acetone:DCM. The resulting organic phase was pipetted off, and the aqueous phase produced during sediment extraction was back-extracted three times with an equivalent volume of hexane. The hexane extract was then added to the organic phase for analysis of PAHs.

Both the sonication-extracted and ASE-extracted samples were rotary evaporated and solvent-exchanged with hexane. The hexane extracts were then subjected to solid–liquid chromatography on precleaned, anhydrous Na_2SO_4, acid and solvent-rinsed elemental copper, and precleaned silica gel (100–200 mesh; 36- × 1.5-cm column) using hexane and DCM to remove organic polymers, elemental sulfur, and aliphatic and polar compounds [12]. The PAH fraction (4:1 hexane:DCM) that eluted from the silica column was again rotary evaporated and solvent-exchanged with hexane, and an internal standard containing deuterated PAHs (d_{10}-phenanthrene, d_{12}-chrysene, and d_{12}-perylene) was added to each extract. The samples were further concentrated under a purified N_2 stream before analysis.

Instrumental analysis

Polycyclic aromatic hydrocarbons were identified and quantified using a gas chromatograph (Hewlett-Packard 5890, Palo Alto, CA, USA) and a mass-selective detector (Hewlett-Packard 5971A) operated in selective-ion monitoring mode. The capillary column used was 30 m in length, with an inner diameter of 0.25 mm (DB-XLB; J&W Scientific, Folsom, CA, USA) and a stationary-phase film thickness of 0.25 μm. Helium was used as the carrier gas at a flow rate of 2 ml min^{-1} and a head pressure of 17 kPa. The temperature program was 100 to 150° at 25°C min^{-1}, 150 to 260° at 6°C min^{-1}, and 260 to 290° at 1°C min^{-1}. The initial oven temperature was 100°C, whereas the injector temperature was 300°C. One microliter of sample was injected in a splitless injection. Each PAH was identified relative to known reference standards (Supelco Mixture 610 and Supelco individual compounds, Bellefonte, PA, USA).

Quality assurance

The sonication-extraction and ASE methods were evaluated using two replicate samples of the National Institute for Standards and Testing (Gaithersburg, MD, USA) Standard Reference Material (SRM) 1944 New York–New Jersey Waterway Sediment. The PAH concentrations for SRM 1944 measured using the sonication-extraction method were significantly lower as a whole than the reported SRM 1944 values (paired *t* test, 95% confidence interval). Percentage differences ranged from 3.6% (benzo[*b*]fluoranthene) to −54% (anthracene), and they averaged −25% (Table 1). However, to prevent artificial elevation of the reported PAH concentrations, the measured values reported here have not been corrected for method extraction efficiency. As a result, the data presented are considered to be conservative. In contrast, PAH levels associated with SRM 1944 determined using the ASE method were not significantly different from the certified SRM 1944 values (paired *t* test, 95% confidence interval), ranging from −34% to 30% and averaging −12% (Table 1). As with the sonication-extracted samples, PAH values determined with the ASE method were not corrected for extraction efficiency.

Twenty-five individual PAHs were detected in each of the sediment samples. Recoveries of the PAH surrogate standards averaged 86.0% ± 8.8%, 106% ± 16%, and 89.2% ± 12% for d_{10}-anthracene, d_{12}-benz[*a*]anthracene, and d_{12}-benzo[*a*]pyrene, respectively. However, because of the extremely high concentrations in many of the sediment samples (as much as 2,500 μg/g dry wt), an independent evaluation was conducted to determine if the surrogate standard could accurately quantify PAH concentrations exceeding the standard concentrations by as much as two orders of magnitude. This evaluation and subsequent data correction are explained in detail elsewhere [11] but are briefly described here. By using constant surrogate concentrations and stepwise increases in PAH concentrations up to two orders of magnitude higher than those of the surrogate, it was determined that calculated PAH concentrations were accurate (±12% of actual) when PAH concentrations were less than 10-fold the surrogate concentrations. However, calculated concentrations exceeded the actual (22–37%) when PAH concentrations exceeded the surrogate compound concentrations by more than 10- to 100-fold. Thus, correction factors were applied to 67 of the 112 sediment samples in which PAH concentrations exceeded surrogate concentrations by 10- to 845-fold. In all cases, levels of individual PAHs were calculated relative to PAH surrogate abundances and, therefore, automatically corrected for recovery.

Particulate organic carbon and nitrogen

Particulate organic carbon (OC) and nitrogen were quantified using a carbon-hydrogen-nitrogen-sulfur-oxygen elemental analyzer (EA 1108; Fison, Beverly, MA, USA). Analyses were conducted on the dried-sediment subsample used to determine water content, which was homogenized using a mortar and pestle. Approximately 20 to 40 mg of homogenized sample were placed into an ashed, silver cup and then weighed. Each sample was acidified with one to four drops of 10% HCl and allowed to dry overnight in a 60°C oven to remove inorganic carbon. The samples were then placed in the analyzer and flash-heated to 1,050°C to convert the organic matter into CO_2, NO_x, and H_2O. Organic carbon and particulate nitrogen are reported on a percentage basis.

Bulk $\delta^{13}C$ analysis

Bulk $\delta^{13}C$ (OC) values were quantified using a Hydra 20-20 stable-isotope analyzer (PDZ Europa, Northwich Cheshire, UK) at the University of California, Davis Stable Isotope Facility (Davis, CA, USA). A subsample of the dried sediment used for water-content analysis was acidified with 10% HCl, completely dried on a hot plate, and thoroughly homogenized. Approximately 20 to 111 mg of sediment were weighed into ashed, tin cups based on the previously determined OC content of the sample. Replicates of every 10th sample were used to evaluate the precision of the analysis (average standard error = 0.04‰).

Grain size

A 20- to 30-g subsample of wet sediment was weighed into a 50-ml Pyrex® beaker. Approximately 10 to 20 ml of surfactant were added to each sample to promote separation of physical aggregates. The sand fraction was determined by sieving the subsample through a 63-μm sieve into a 1,000-ml, graduated cylinder and then transferring the fraction remaining in the sieve to a preweighed, aluminum weighing boat. The liquid volume in the graduated cylinder was brought up to 1,000 ml with deionized water. The silt and clay size fractions were determined by stirring the suspension in the graduated cylinder, then removing 20-ml subsamples at 20 s and at 2 h, respectively, and placing the subsamples into preweighed, aluminum weighing boats. The sand, silt, and clay fractions were then calculated using the dried weights of each fraction (corrected for the contribution of the surfactant) [13].

RESULTS AND DISCUSSION

Summary of PAH concentrations

Twenty-five individual PAHs were analyzed in each sediment sample. Total PAH concentrations (ΣPAH) were calculated as the sum of all quantifiable PAHs (fluorene + 1-methylflourene + phenanthrene + anthracene + 2-methylphenanthrene + 2-methylanthracene + 1-methylanthracene + 1-methylphenanthrene + fluoranthene + pyrene + benz[a]anthracene [B*a*A] + chrysene + benzo[*b*]fluoranthene [B*b*F] + benzo[*k*]fluoranthene + benzo[*e*]pyrene + benzo[*a*]pyrene [B*a*P] + perylene + indeno[1,2,3,*cd*]pyrene [IP] + benzo[*ghi*]perylene [B*ghi*P]) expressed as micrograms per gram sediment (μg/g) on a dry-weight basis. Large spatial variation in PAH concentrations was observed throughout the sampling area, both within the channel and shoal regions as well as between these two areas. Total PAH concentrations of surface sediments ranged from 0.035 to 1,730 μg/g; the maximum subsurface (2- to 4-cm layer) sediment concentration exceeded 2,500 μg/g. Within the Elizabeth River channel, ΣPAH concentrations ranged from 0.953 to 57.3 μg/g; channel samples collected in the main stem did not exceed 6 μg/g. The ΣPAH in shoal samples ranged from 0.035 to 1,730 μg/g. The highest concentrations were observed in samples collected in the shoal areas adjacent to the former wood-treatment facilities, the Atlantic Wood (Portsmouth, VA, USA; maximum ΣPAH, 740 μg/g) and the Eppinger and Russell (Chesapeake, VA, USA; maximum ΣPAH, 1,730 μg/g), both located adjacent to the southern branch of the Elizabeth River. Nonaqueous-phase liquids were observed during the collection of samples from these two areas, identified by visible oil sheen on the sediment. In contrast, the highest sediment PAH concentration in the main stem was located at E01 (51.5 μg/g) (Fig. 1B), in the shoal area adjacent to the suspected location of a former coal gasification plant. As with the shoal areas, the highest PAH levels in channel sediments were located in the southern branch, specifically immediately downriver of the former Eppinger and Russell wood-treatment facility (57.3 μg/g).

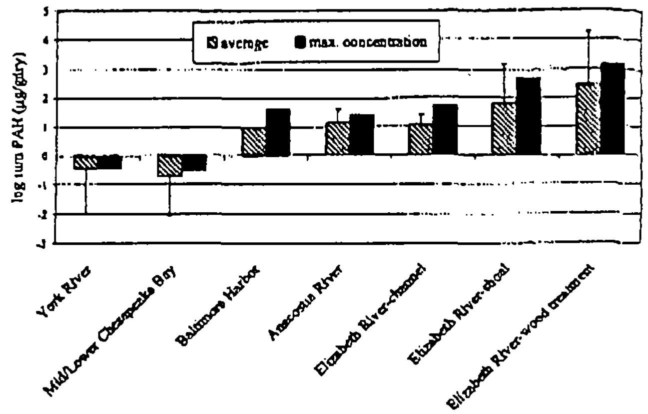

Fig. 2. Comparison of average and maximum Σpolycyclic aromatic hydrocarbon (PAH) values for the Elizabeth River channel, the Elizabeth River shoal, and the Elizabeth River wood-treatment shoal areas from the present study and the Anacostia River [16], Baltimore Harbor [15], the mid/lower Chesapeake Bay [14], and York River [14]. Error bars represent the log standard error. See Figure 3 for locations.

Sediment PAH concentrations in the shoal regions of the Elizabeth River, excluding designated source-specific shoal samples, exceed those of the York River (VA, USA) and lower Chesapeake Bay, two nonindustrial areas, by more than two orders of magnitude, whereas the average channel ΣPAH concentration in the Elizabeth River exceeds the York River and lower Chesapeake Bay values [14] by more than an order of magnitude (Fig. 2). The average ΣPAH concentration in shoal regions of the Elizabeth River exceeds the average total for

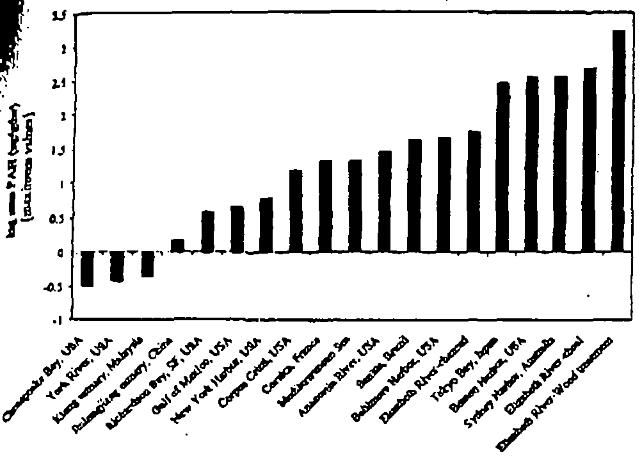

Fig. 3. Comparison of maximum Σpolycyclic aromatic hydrocarbon (PAH) concentrations for the Elizabeth River channel, the Elizabeth River shoal, and the Elizabeth River wood-treatment shoal areas from the present study and the mid/lower Chesapeake Bay [14], York River [14], Klang River estuary [34], Jiulongjiang estuary [35], Richardson Bay [36], Gulf of Mexico [37], New York Harbor [38], Corpus Cristi [37], Corsica [39], Mediterranean Sea [39], Anacostia River [16], Santos [40], Baltimore Harbor [15], Tokyo Bay [34], Boston Harbor [41], and Sydney Harbor [42]. Note that the number of individual PAHs contributing to the reported ΣPAH may differ from the ΣPAH reported in the present study.

both Baltimore Harbor and the Anacostia River [15,16], the two other regions of concern in the Chesapeake Bay system (http://www.chesapeakebay.net/bayfaq.htm), by more than a factor of four. However, the average channel ΣPAH concentration in the Elizabeth River is not significantly different ($p > 0.05$) from the average values for both Baltimore Harbor and the Anacostia River. Samples collected in the vicinity of two former wood-treatment facilities in the southern branch of the Elizabeth River exhibited elevated average ΣPAH concentrations when compared to the ΣPAH concentrations from the nonsource-specific shoal samples in the Elizabeth River and the two other regions of concern in Chesapeake Bay. The ΣPAH concentrations in the source-specific sediment samples exceeded those in the remaining shoal samples by a factor of four and exceeded the ΣPAH values in the Baltimore Harbor and the Anacostia River by more than an order of magnitude.

Sediment PAH concentrations were also examined relative to representative coastal and estuarine systems in the United States and around the world (Fig. 3). Maximum Elizabeth River ΣPAH concentrations in nonsource-specific shoal regions are comparable to those observed in Tokyo Bay (Japan), Sydney Harbor (Australia), and Boston Harbor (USA), whereas the maximum ΣPAH concentrations observed in the vicinity of the two former wood-treatment facilities exceeded the maximum values observed elsewhere around the world. This list of contaminated coastal and estuarine systems is not exhaustive, but it is evident that sediments in the Elizabeth River as a whole, and particularly in the vicinity of the two former wood-treatment facilities, are highly impacted.

In addition to higher overall PAH concentrations in Elizabeth River sediments, consistently and significantly ($p < 0.05$) higher percentages of carcinogenic PAHs (B*b*F and B*a*P) [17] were observed compared with either the York River or the lower Chesapeake Bay (Fig. 4). Conversely, the percentage of perylene, a PAH associated predominantly with natural or diagenetic formation [18], was five- to sixfold lower in the Elizabeth River compared with the more pristine areas, indicating that the anthropogenic input of PAHs, to the Elizabeth River dominates PAH influx to the system.

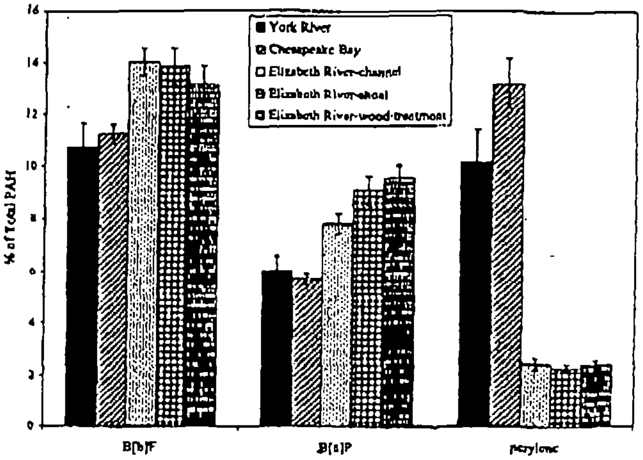

Fig. 4. Comparison of representative carcinogenic compounds (benzo[*b*]fluoranthene [B*b*F] and benzo[*a*]pyrene[B*a*P]) and perylene between the Elizabeth River channel, shoal, and wood-treatment shoal areas in the present study and the mid/lower Chesapeake Bay and York River [14]. Error bars represent the standard error. All study sites are located in the United States. PAH = polycyclic aromatic hydrocarbon.

Contaminant transport

Bieri et al. [10] reported a decreasing logarithmic ΣPAH concentration gradient along the channel from the former wood-treatment facility (Atlantic Wood) at Eppinger and Russell to Craney Island at the mouth of the Elizabeth River. Bieri et al. [10] speculated that diffusion–advection was controlling the distribution of PAH-contaminated sediments throughout the Elizabeth River, thus implicating large spills from the former wood-treatment facilities of the southern branch in contamination of the main stem of the estuary. However, the sample locations from the 1986 investigation did not extend beyond the Eppinger and Russell site [4]. To evaluate the current pattern of PAH distribution in channel sediments, the channel ΣPAH data were plotted as a function of distance (river kilometer from mouth) (Fig. 5A). This plot depicts a diffusional profile for PAHs away from a source in the southern branch centered approximately 17.8 km from the mouth of the river. Diffusion of a substance away from a plane source can be modeled using the following equation [19]:

$$C = \frac{M}{2(\pi D t)^{1/2}} e^{-x^2/4Dt} \qquad (1)$$

where C is the concentration, M is the mass deposited at the source at time $t = 0$, x is the distance from the source, and D is the diffusion coefficient for the substance. When the channel ΣPAH data are plotted using a linearized form of the above equation with the PAH source centered at 17.83 km, a significant regression is observed, which explains 69% of the variability in the data (Fig. 5B). The sample at 17.8 km (E23) was collected in a region between two former wood-treatment facilities with known or suspected historical releases of creosote [4,5]. Thus, the creosote source(s) in this region of the Elizabeth River likely is an important contributor to PAH contamination in the estuary. However, the variability in the data indicates that this is not the only PAH source to the Elizabeth River sediments.

Closer examination of the diffusional profile of individual

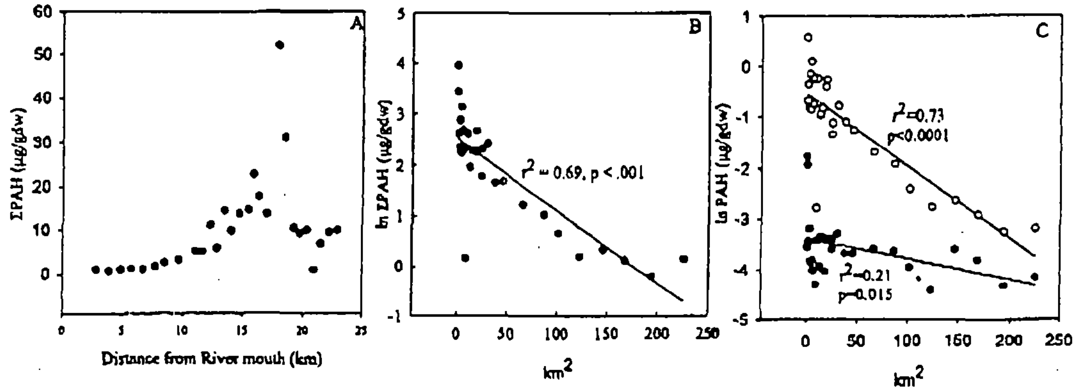

Fig. 5. Polycyclic aromatic hydrocarbon (PAH) values for channel samples. (A) ΣPAH for channel samples from mouth of Elizabeth River (USA) to river kilometer 24. (B) Profile of ln ΣPAH versus km² based on a diffusional model. (C) Profile of ln [PAH] versus km² based on a diffusional model for benzo[*ghi*]perylene (B*ghi*P; ○) and 1-methylfluorene (●).

PAHs in Elizabeth River channel samples reveals equivalent trends for 2-methylanthracene and parent PAHs except for perylene (Fig. 5C). Perylene, 1-methylfluorene, 2-methylphenanthrene, 1-methylanthracene, and 1-methylphenanthrene all had significantly lower slopes (−0.0042 to −0.0093; $p < 0.05$) and r^2 values (0.21–0.48) than the remaining PAH (slope range, −0.011 to −0.017; r^2 range, 0.43–0.77). Based on Equation 1, lower slopes ($1/4Dt$) would indicate higher diffusion coefficients for some PAHs, which is unlikely given that turbulent rather than molecular diffusion would dominate the dispersion of sediment-associated PAHs. Moreover, given that desorption of organic pollutants from sediments typically decreases with increasing molecular weight and hydrophobicity within a class of compounds [20], more rapid desorption of perylene and, hence, a higher apparent diffusion coefficient compared to the other high-molecular-weight PAHs would not be expected. More likely, the lower slopes and low values for r^2 for the methyl-PAHs (Fig. 5C) and perylene indicate additional sources of these compounds to Elizabeth River sediments, such as biogenic sources (for perylene [18]) or petrogenic sources (see, e.g., [5]). The presence of secondary sources of PAHs to sediments in the southern branch is consistent with source-apportionment modeling using isomer ratios [11].

PAH–particle property relationships

Polycyclic aromatic hydrocarbon concentrations often are closely correlated with the OC content and clay content of sediment [21,22]. This correlation is thought to result from the hydrophobic nature of the compounds and their affinity for organic matter [20,23]. The general survey samples were examined to determine any relationships between ΣPAH and geochemical parameters given that these samples cover a greater geographical range of the Elizabeth River and are not focused on target PAH source areas. However, when ΣPAH and individual PAHs from the survey samples were examined relative to sediment OC content, no useful correlation was found (highest $r^2 = 0.30$), unlike previous reports concerning phenanthrene, anthracene, and four-and five-ring PAHs ($r^2 = 0.86$) [21]. Including the source-specific samples (i.e., those collected from targeted, suspected or potential source areas in the southern branch) did not significantly improve the relationship ($r^2 = 0.24$). Separation of samples based on carbon:nitrogen ratios, using carbon:nitrogen values of less than 12 as indicative of typical estuarine organic matter [24], also failed to produce a significant relationship between sediment OC and ΣPAH. As a result, sediment OC content could not be used to model and predict ΣPAH concentration in Elizabeth River sediments. Likewise, no significant relationships were observed between sediment ΣPAH and the individual PAH, and clay content of sediments (highest $r^2 = 0.007$).

In a study of sediments in several South Carolina estuaries, PAH distributions in the sediments were not controlled by sediment type, total OC, or percentage of fine-grained sediment. Instead, PAH distributions in sediments were largely influenced by the proximity of PAH sources, which ranged from agricultural to industrial [25]. Near PAH sources in the Elizabeth River, an improved relationship between OC and ΣPAH was observed in the vicinity of a coal-fired power plant ($r^2 = 0.48$). The ΣPAH in sediments near one of the former wood-treatment facilities (Atlantic Wood) demonstrated a strong relationship with OC ($r^2 = 0.70$); however, this was not observed at the other former wood-treatment facility (Eppinger and Russell) ($r^2 = 0.20$), thus precluding the use of OC as a predictor of ΣPAH for this general source type.

Although no particle property was observed to be correlated with sediment PAH content, one parameter may be a useful screening tool to indicate PAH contaminated sediments in the Elizabeth River. All highly contaminated sediments were observed to fall in a relatively narrow range of bulk $\delta^{13}C$ of OC (−24.3‰ ± 0.5‰) (Fig. 6). However, even though average $\delta^{13}C$ values for sediments collected in the vicinity of the two former wood-treatment facilities were very similar (Atlantic

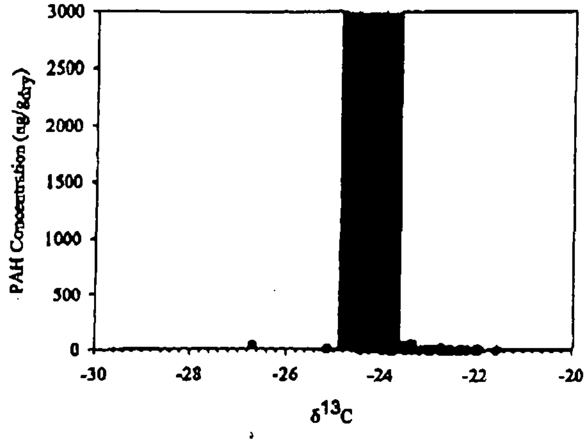

Fig. 6. Comparison of Σpolycyclic aromatic hydrocarbon (PAH) and bulk $\delta^{13}C$ (total organic carbon) values for all sediments.

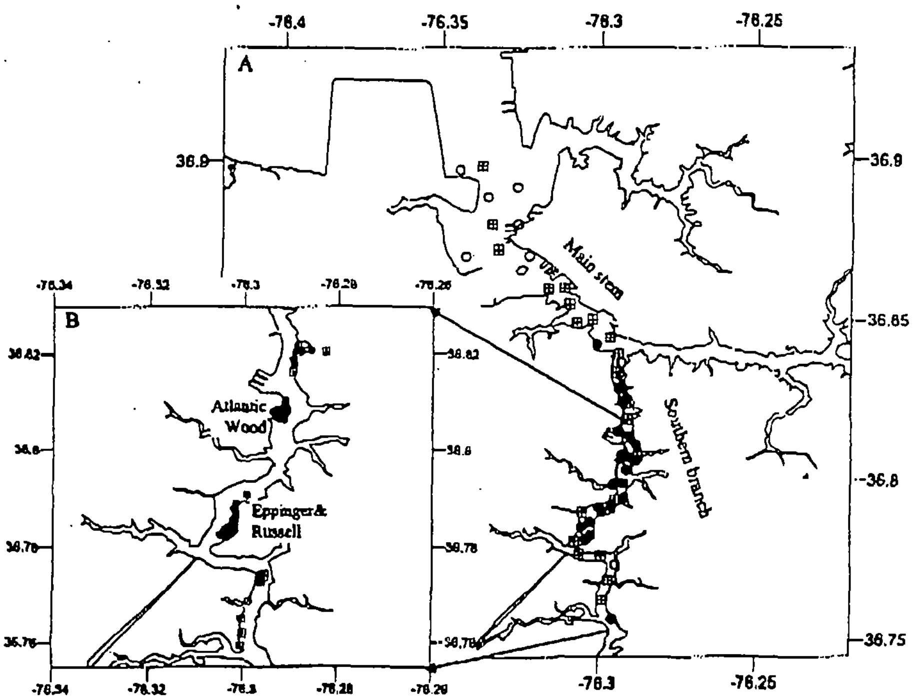

Fig. 7. (A) Effects levels for the samples collected from the Elizabeth River (USA). Open circles indicate samples with polycyclic aromatic hydrocarbon (PAH) concentrations below the effects range low (ERL); marked squares are samples with PAH concentrations between the ERL and the effects range median (ERM); black circles are samples with PAH concentrations exceeding the ERM. (B) Effects levels for samples collected from the Elizabeth River targeted source areas.

Wood, −24.05‰ ± 0.24‰; Eppinger and Russell, −24.04‰ ± 0.49‰), numerous lesser-contaminated sediments had similar $\delta^{13}C$ values. Because the Atlantic Wood and the Eppinger and Russell sediments had $\delta^{13}C$ values that were not significantly different from the remaining shoal samples in the southern branch, the $\delta^{13}C$ of −24.3‰ ± 0.5‰ may simply reflect organic matter sources in this region of the river and not creosote contamination. The $\delta^{13}C$ values observed here fall within the range of values of bulk OC observed in other estuarine systems [26]. Additional investigations in other creosote-impacted urban estuaries may clarify the utility of $\delta^{13}C$ as a screening tool for PAH contaminated sediments.

Evaluating potential toxic effects

The effects range low (ERL) and effects range median (ERM) are biological effects classifications developed by Long et al. [27] based on contaminant modeling, laboratory assays, and field toxicity studies generated from a review of the toxicological literature. The ERL is the value at which toxicity may begin to be observed in sensitive species; the ERM is the median concentration at which toxic effects should first be observed (http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.pdf). When using ERL and ERM values to evaluate the potential biological effects of PAHs in Elizabeth River sediment, three categories were used: Levels that did not exceed the ERL or that had minimal effects (<ERL); levels between the ERL and the ERM, which have possible effects (>ERL and <ERM); and levels that exceed the ERM, which have probable effects on benthic biota (>ERM) (Fig. 7). The ERL and ERM values do not account for biological effects induced by site-specific processes, but these values do provide a useful first approximation of potential biological effects.

Apart from one sample collected in the vicinity of a suspected former coal gasification site, Elizabeth River main-stem sediments did not exceed the ERM for individual PAHs or ΣPAH (Fig. 7B). Channel sediment samples within the southern branch are highly variable in terms of the observed PAH effects levels, but in only one instance is the ERL not exceeded (E32, a sandy sediment located in the most upstream area studied). Channel samples located downstream of Atlantic Wood and upstream of Eppinger and Russell, two former wood-treatment facilities, generally fall between the ERL and ERM. Channel samples located adjacent to or between the two former wood-treatment facilities exceed the ERM with only one exception (E20) (Fig. 1B). Likewise, shoal samples collected immediately adjacent to the two former wood-treatment facilities exceeded the ERM with only one exception (P19). Shoal samples collected from the mouth of the southern branch upstream, toward Atlantic Wood, increased in concentration and effects levels, proceeding from less than the ERL near the mouth to greater than the ERM approaching Atlantic Wood, whereas samples collected in the area between the two former wood-treatment facilities varied between greater than the ERL and less than the ERM to greater than the ERM. The potential for significant biological impact in the shoal areas of the two former wood-treatment facilities is further supported when the data are examined using sediment-quality guidelines (SQGs) derived by DiToro and McGrath [28]. These SQGs, based on the assumption of equilibrium partitioning, are exceeded in the shoal regions of Atlantic Wood (three locations) and, to a much greater extent, in those of Eppinger and Russell (11 locations, as well as one in the immediate downstream shoal area). The coal gasification site (E01), located in the main stem, also exceeded the SQGs (for pyrene).

The exceedances of sediment-quality criteria also indicate the impact of point sources in contributing to the overall levels of contamination in the Elizabeth River. These results correspond to toxicological investigations into the biological effects of contaminants in this highly contaminated urban estuary.

Table 2. Environmental half-lives ($t_{1/2}$) calculated from select channel samples of the current data set and concentrations reported by Huggett et al. [2][a]

Polycyclic aromatic hydrocarbon	Sample												
	E47	E49	E41	E39	E38	E36	E03	E04	E06	E07	E14	E17	E23
PHE	NC	NC	12.0	NC	14.1	11.3	11.2	NC	NC	7.6	14.7	NC	6.0
FLRN	NC	12.8	7.2	NC	14.3	8.7	8.8	NC	NC	7.3	13.9	NC	6.0
PYR	NC	15.6	6.7	24.7	12.2	9.5	9.3	NC	NC	8.1	16.2	NC	7.3
B*a*A	NC	11.6	6.8	NC	13.0	9.9	11.7	NC	NC	9.3	NC	NC	8.5
CHRY	12.9	7.0	5.5	15.1	8.5	6.7	9.6	NC	NC	7.8	13.3	NC	8.0
B*b*F	NC	NC	12.3	NC	NC	NC	NC	NC	NC	NC	NC	7.3	14.3
B*e*P	NC	9.5	6.5	9.2	11.4	9.4	10.1	17.5	NC	9.8	10.8	NC	13.5
B*a*P	NC	10.3	6.2	10.2	11.9	11.0	14.1	NC	NC	13.0	21.9	NC	12.4
IP	NC	NC	6.8	12.9	NC	NC	NC	NC	NC	NC	NC	6.1	NC
B*ghi*P	NC	NC	6.1	11.2	NC	NC	NC	NC	NC	NC	NC	4.4	NC

[a] NC denotes no change; underlined values indicate doubling times. PHE = phenanthrene; FLRN = fluoranthene; PYR = pyrene; B*a*A = benzo[*a*]anthracene; CHRY = chrysene; B*b*F = benzo[*b*]fluoranthene; B*e*P = benzo[*e*]pyrene; B*a*P = benzo[*a*]pyrene; IP = indeno[1,2,3-*cd*]pyrene; B*ghi*P = benzo[*ghi*]perylene.

External and internal fish lesions were associated with the high contaminant levels at Eppinger and Russell and immediately downstream [9]. Previous studies indicated toxicological impacts at Atlantic Wood despite only moderate PAH concentrations at that location at the time [2,9]. Current toxicological monitoring efforts in the Elizabeth River involve benthic community assessments and pelagic histopathologic evaluations. Assessments of the benthic community indicate that these sites range from degraded to severely degraded; the region between two of the most heavily contaminated areas (Atlantic Wood and Eppinger and Russell) has the most degraded ranking in the southern branch [29]. An examination of the liver histopathology of a nonmigratory fish species (***Fundulus heteroclitus***) indicated that Atlantic Wood had among the highest incidence of altered hepatocellular foci and neoplasms and was ranked as a severe problem area [30].

As a comparison to PAH levels and potential impact in other systems, a recent sediment toxicity study [31] in the Baltimore Harbor–Patapsco River revealed only one site exceeding the ERM for the compounds analyzed in the present study. Specifically, phenanthrene, pyrene, B*a*A, and B*a*P all exceeded their ERM values for this site, which was located in the Inner Harbor area. Other ERM exceedances were noted in the study (2-methylnaphthalene, acenaphthylene, acenapthene, Σpolychlorinated biphenyls, and several metals). The majority of the Baltimore Harbor–Patapsco River sites were greater than the ERL and less than the ERM for the PAHs in question.

PAH concentration change over time

Using sediment PAH concentrations measured in a 1983 survey of the Elizabeth River [2], the change in PAH concentrations over time for various channel locations was evaluated. In areas where the sampling sites were approximately the same for the two surveys, first-order rate constants and PAH environmental half-lives in channel sediments were calculated as

$$[\ln(C/C_o)]/t = -\lambda \qquad (2)$$

where C is the concentration of an individual PAH from this investigation, C_o is the concentration of an individual PAH from the 1983 sampling [2], t is the time between sampling events, and λ is the first-order rate constant. This model assumes that the system is at steady state and is unaffected by mixing. However, given the estimated accuracy of the PAH concentrations (Table 1), changes of less than ±50% in sediment PAH concentrations were considered to be insignificant. In such cases, sediment PAH levels had no significant increases or decreases in concentration during the 15-year interval from 1983 to 1998.

For most of the Elizabeth River channel sites assessed, PAH concentrations decreased over time, with environmental half-lives ranging from 5 to 25 years (Table 2). This indicates that weathering or degradation processes or, perhaps, physical processes (mixing, bioturbation, and more likely, dredging) are effective in reducing contaminant loads to surface sediments. It also indicates that any additional inputs either are limited or are adding PAHs to the system at a rate lower than the removal rates for these select channel locations. However, significant decreases in most PAH concentrations were not detected at four sites (E04, E06, E17, and E47) (Table 2 and Fig. 1B), and one of these sites, E17, which is located between Atlantic Wood and Eppinger and Russell, demonstrated an increase in the concentrations of B*b*F, IP, and B*ghi*P. Two of the sites where significant decreases were not observed (E04 and E06) are located downstream of Atlantic Wood, in the southern branch of the Elizabeth River. Historical and potential current inputs from the wood-treatment facility combined with any current point- or nonpoint-source input (e.g., input from ship maintenance activities or other current industrial activities) may occur at a rate equivalent to the removal processes in this region. Likewise, the selective increases in PAH concentrations at E17, which is located between two known former wood-treatment plants, may result from contaminant accumulation proceeding faster than the removal processes at this site. This may be expected of the heavier compounds (e.g., B*b*F, IP, and B*ghi*P), which tend to degrade [32] and desorb slowly [20].

The area of increased PAH concentrations in Elizabeth River sediments likely is caused by the joint contributions of former wood-treatment facilities, including Atlantic Wood, Eppinger and Russell, and potentially, Republic Creosote, which historically was located between the two other wood-treatment sites [5]. High PAH concentrations in the shoal areas of both Atlantic Wood and Eppinger and Russell as well as the presence of a nonaqueous-phase liquid phase during sample collection at these sites indicate substantial releases of PAHs. Tidal flushing, although limited in the Elizabeth River, as well as indirect impacts of ship traffic and dredge activities may aid in the dispersal of contaminants from the sites.

Using the environmental rate constants derived for the varous PAHs at select sites, the estimated time for contaminant levels to decrease to the ERL values for these channel locations was calculated. As indicated above, all samples collected in the main stem with calculated environmental half-lives are currently at or below the ERL. Four sites (E03, E07, E14, and E23) had estimated times to achieve the ERL ranging from 2 to 42 years. In general, clean-up times for these channel locations increased with progression toward the more highly contaminated area of the southern branch, with an average time of four years at E03 to an average time of 29 years at E23. With the exception of chrysene, clean-up times for individual PAHs typically increased with increasing molecular weight. Chrysene also had a shorter clean-up time than its isomer, B*a*A. This may result, in part, from the much greater gas efflux of chrysene compared to B*a*A from the Elizabeth River [33]. These estimates provide useful information on contaminant changes over time for the channel locations, taking into consideration the different analytical techniques and the similar (but not identical) sample locations in the two studies, but similar estimates are not available for the more highly impacted shoal locations.

CONCLUSION

Extremely high PAH levels relative to the other two designated regions of concern in the Chesapeake Bay system, as well as coastal and estuarine systems worldwide, are observed in Elizabeth River sediments. Nonetheless, comparison of channel samples between the current data set and those data sets collected during the early 1980s demonstrates a general trend toward reduction in PAH concentrations; however, steady-state and increased sediment PAH concentrations in the vicinity of two former wood-treatment facilities were noted. Moreover, it is unlikely that sediment PAH concentrations in the highly impacted shoal regions of the Elizabeth River have declined significantly since the historical releases of creosote occurred, because no dredging or clean-up efforts have been focused on these areas.

Based on examination of the contaminant levels in the main stem and southern branch of the Elizabeth River using established criteria, this river remains a clear hazard to benthic and pelagic species. Despite continual dredging of the channel, PAH concentrations in the river have not been reduced to nonhazard levels. The southern branch is most notable in its level of contamination. Because of the low flushing of the river [7–9], PAHs associated with sediment resuspended through dredging and normal ship traffic are unlikely to be removed from the Elizabeth River and have a higher probability of settling within the river. This may help to explain the consistently high PAH concentrations found in the sediments in the vicinity of former wood-treatment facilities. Additionally, contamination ascribed to discrete, large, historical releases is not the only source of PAHs to the river. Suspected continual discharges from former wood-treatment facilities, current and historical petroleum and coal transport, and current coal usage also may be contributing to the elevated PAH concentrations [5,11].

The influence of point sources of PAHs in the southern branch of the Elizabeth River was evident in examining the geochemical parameters of the sediment (%OC, %clay, and C/N). The lack of useful correlation of PAHs to standard geochemical (OC, clay, and C/N) parameters indicates the importance of separate forcings (i.e., source type and proximity) on PAH distributions in Elizabeth River sediments. The PAH distribution observed in this investigation is a clear departure from classic organic contaminant–organic matter associations and requires additional investigation concerning the role of source type, both historical and current, in PAH distribution in the estuary.

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